



Research Article

Training β relaxation to rejuvenate metallic glassesL.T. Zhang^a, Yun-Jiang Wang^{b,c}, Y. Yang^{d,e}, J.C. Qiao^{a,f,*}^a School of Mechanics, Civil Engineering and Architecture, Northwestern Polytechnical University, Xi'an 710072, China^b State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China^c School of Engineering Science, University of Chinese Academy of Sciences, Beijing 100049, China^d Department of Mechanical Engineering, College of Engineering, City University of Hong Kong, Tat Chee Avenue, Kowloon Tong, Kowloon, Hong Kong SAR, China^e Department of Materials Science and Engineering, College of Engineering, City University of Hong Kong, Tat Chee Avenue, Kowloon Tong, Kowloon, Hong Kong SAR, China^f Innovation Center, NPU-Chongqing, Chongqing 401135, China

ARTICLE INFO

Article history:

Received 20 January 2023

Revised 22 February 2023

Accepted 24 February 2023

Available online 4 April 2023

Keywords:

Metallic glass

 β relaxation

Rejuvenation

Structural heterogeneity

ABSTRACT

In the current work, we demonstrated that the rejuvenation of metallic glasses can be achieved through training the β relaxation process. With the increase in the training frequency, a transition from structural relaxation to rejuvenation can be observed. This rejuvenation treatment is unexpected due to it occurs at a relatively small cyclic strain of 0.2%. Rejuvenation is beneficial to increase the relaxation enthalpy and promotes the decoupling of the β relaxation process and α relaxation process. A cluster of β relaxation time curves are formulated to describe any energetic state between ultrastable and ultimately rejuvenated metallic glasses. In addition, rejuvenation expands the distribution of β relaxation process, anelastic and viscoplastic components during the deformation process.

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1. Introduction

Metallic glasses (MGs) possess disordered atomic structures and are of out-of-equilibrium nature. Therefore, spontaneous structural relaxation occurs since they have been prepared, deteriorating their initial mechanical and physical properties [1–5]. Naturally, the exploration of structural rejuvenation – the reverse process of structural relaxation – in MGs is an important subject of materials science and solid mechanics because the structural rejuvenation behaviors of amorphous solids open a new avenue for improving the mechanical/physical properties [6–9].

Recently, abundant strategies to achieve rejuvenation have been systematically developed, such as cold-rolling, elastostatic loading, irradiation, cryogenic thermal cycling, mechanical cycling, and high-pressure torsion [10–14]. The highly rejuvenated MGs can be prepared by severe plastic deformation [9]. However, the severely deformed sample is actually a composite material composed of the “shear bands” and the “undeformed glassy matrix”. The complexity of structure brings interference to the study of the structure and properties of the rejuvenated glassy materials. Cryogenic thermal cycling is non-destructive and homogenous to rejuvenate MGs and

is applicable to any size of glass sample [8]. In addition, the degree of rejuvenation of MGs obtained by this method appears limited compared to other mechanical treatments [15,16]. Up to now, the maximum increase of relaxation enthalpy of MGs after cryogenic thermal cycling treatment is only 0.7 kJ mol⁻¹ [17]. It has been accepted that heating an MG into the supercooled liquid region and then rapidly cooling can recover the relaxation enthalpy [18]. One can expect that global rejuvenation by such a method requires a high cooling rate, at least greater than the cooling rate during the formation process. The above strategies have considerable advantages, but they either involve multiple steps, are destructive or lead to a possible change in shape, or have difficulty in accessing the radiation facilities. On the other hand, a part of these methods not only brings about rejuvenation but also produces an unexpected side effect of harmful structural relaxation and even crystallization [19,20]. Even though there have been plentiful developments towards the achievement and understanding of the nature of rejuvenation, an effective method to rejuvenate MGs is still urgently needed.

Dynamic mechanical relaxation is one of the intrinsic features of amorphous solids, which contributes to various behaviors in glass systems [21–23]. Glassy materials display two main dynamic mechanical relaxation processes, i.e., the main α relaxation and secondary β relaxation (also called Johari-Goldstein relaxation) [1]. The α relaxation is activated in the supercooled liquid region, but

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frozen below the glass transition temperature T_g [1]. Additionally, it is closely associated with the dynamic glass transition, i.e., irreversible large-scale cooperative atomic/molecular rearrangements [24]. It is shown that rejuvenation by mechanical methods significantly strengthens the signal of β relaxation and promotes the degree of the structural heterogeneity of MGs [25]. In comparison, the effect of cryogenic thermal cycling on β relaxation strongly depends on the chemical composition of MGs, i.e., only slight strength in a La-based MG [8] but apparent improvement in a Fe-based MG [26]. All these brilliant achievements reveal promising strategies of modulation the mechanical properties of MGs. They also concentrate on the effect of rejuvenation on mechanical relaxations, but ignore another vital issue: what is the interdependence between rejuvenation and β relaxation? Is it possible to rejuvenate and achieve elaborate tailoring of the mechanical behaviors of MGs by the β relaxation process?

To exactly answer this question, the top priority is the establishment of the correlation between the β relaxation and the mechanical properties of MGs. Yu et al. [27] accomplished tensile plasticity in a $\text{La}_{68.5}\text{Ni}_{16}\text{Al}_{14}\text{Co}_{1.5}$ MG near room temperature by activating β relaxation. Importantly, cryogenic thermal cycling promotes the separation of β relaxation and introduces a large tensile plasticity in a Fe-based MG, which confirms the feasibility of rejuvenation by activating β relaxation [26]. Therefore, the training of β relaxation is one of the necessary conditions for controlling the plasticity of MGs. It is noted that recent molecular dynamics (MD) simulations further support the possibility of the rejuvenation of MGs via activating the β relaxation. Yuan et al. [28] reported that the random removal of atoms from the glassy matrix accelerates the formation of atomic clusters with high displacement. This allows the initiation of the β relaxation such that the rejuvenation dominates the dynamic behavior. Similar MD simulation results have been recently reported by Li et al. [29], who altered the β relaxation from an excess wing to shoulder by tailoring spatial heterogeneities of an MG. These proceeding facts inspire us to employ β relaxation to rejuvenate MGs and provide a comprehensive theoretical understanding from a kinetic aspect.

This paper aims to train the β relaxation process to achieve structural rejuvenation of MGs and give deeper insight into the regulatory mechanism of the rejuvenation on the structural/dynamic heterogeneity of such amorphous materials alike. Based on the experimental and theoretical analysis, we provide strong evidence of rejuvenation by the β relaxation training. The input energy during periodic loading reactivates the reversible β relaxation and rejuvenates MGs. One of the signals of rejuvenation is the decrease of the characteristic activation energy of the β relaxation, which is beneficial from the increasing training frequency. The rejuvenation enhances the atomic mobility and promotes the decoupling of the β relaxation from the α relaxations. The increase of the training frequency also broadens the distributions of the relaxation times of the β relaxation, anelastic and viscoplastic components of deformation under creep loading.

2. Experimental procedures

2.1. Sample preparation

A master alloy with the chemical composition of $\text{La}_{30}\text{Ce}_{30}\text{Ni}_{10}\text{Al}_{20}\text{Co}_{10}$ (at.%) was prepared by arc-melting pure metals in the high-purity argon atmosphere [30]. To scavenge oxidation during the process, a titanium getter was employed. The master alloy was then re-melted at least six times to ensure its chemical homogeneity at a medium- or long-range length scale. A single roller melt-spinning technique was used to prepare ribbons with a width of 1.2 mm and a thickness of 30 μm .

2.2. Training of the β relaxation process

Let us suppose the applied stress $\sigma(t)$ evolves sinusoidally with time t :

$$\sigma(t) = \sigma_0 \sin(\omega t) \quad (1)$$

Here, ω is the angular frequency. Generally, the real-time strain response of the glassy materials should be also sinusoidal in time, but it will lag the applied stress by a period $\Delta t = \delta/\omega$, where δ is the phase angle such that

$$\varepsilon(t) = \varepsilon_0 \sin(\omega t - \delta) \quad (2)$$

As a result of the phase lag between the applied stress and the responsive strain, the dynamic stiffness can be treated as a complex number E^* . “Dynamic” in this context refers to oscillatory input rather than the inertial effects:

$$E^* = \frac{\sigma(t)}{\varepsilon(t)} = E' + iE'' \quad (3)$$

E' is the storage modulus, which is related to the elastic response of glassy systems. E'' is the loss modulus, which is closely associated with the viscoelastic response. Here different driving frequencies of 0.01, 0.1, 1, and 10 Hz were employed to train the β relaxation process. The samples were heated to 383 K at a heating rate of 3 K min^{-1} (the reason for the selected temperature and frequency is explicated below).

On the premise of training the β relaxation process, the thermal property of MGs was confirmed by a differential scanning calorimeter (DSC, NETZSCH 449 C) at a heating rate of 20 K min^{-1} . Mechanical spectroscopy experiments were carried out in two modes in a commercial dynamic mechanical analyzer (DMA, TA Q800): (i) single frequency, the samples were heated to 473 K with a constant heating rate of 3 K min^{-1} and the constant driving frequency is 1 Hz; (ii) multiple frequencies, the samples were heated to 423 K with a constant heating rate of 2 K min^{-1} . In this condition, the driving frequencies are 1, 2, 4, 8, and 16 Hz, respectively. The creep experiments were performed at 403 K in DMA. The applied stress is 25 MPa and the temperature was held constant for 10 min to ensure that thermal equilibrium is obtained prior to the creep tests.

3. Results and discussion

Structural heterogeneity has been confirmed as an inherent feature of MGs by means of experiment, theoretical analysis as well as simulation methods [2]. In the concept of the flow units proposed by Wang et al. [1], the structure of MGs can be modeled as flow defects (liquid-like regions) surrounded by the glass matrix (solid-like regions). In the complex plane, the storage modulus and the loss modulus can be expressed as:

$$E' = \frac{\sigma_0}{\varepsilon_0} \cos\delta, \quad E'' = \frac{\sigma_0}{\varepsilon_0} \sin\delta \quad (4)$$

Therefore, Eq. (2) can be rewritten as

$$\sigma(t) = \varepsilon_0(E' \cos\omega t - E'' \sin\omega t) \quad (5)$$

Eq. (5) is a typical parametric equation for an ellipse, that is, they trace out an ellipse for values of t , and the stress-strain curve for oscillatory stress is an elliptic hysteresis loop. The work done in stressing a material (per unit volume) is given by:

$$\Delta W = \oint_0^{t_0} \sigma d\varepsilon = \oint_0^{t_0} \varepsilon_0^2 (E' \sin\omega t \cos\omega t + E'' \cos^2\omega t) dt \quad (6)$$

Here t_0 is an arbitrary time. For the glass matrix or solid-like region, the storage energy is totally elastic, and strain releases

when stress is removed, i.e., the input energy is not stored in the solid-like regions. It can be expected that the input energy drives the atomic rearrangements and the transition of the energetic state. For one complete cycle, the input energy ΔW_0 is readily obtained by the area of the ellipse as $\Delta W_0 = \pi E'' \varepsilon_0^2$.

Based on the similarity between amorphous polymers and MGs, the fluctuation of entropy and enthalpy at the microstructural scale is a pretty visualization of the structural heterogeneity of MGs [31]. These regions possess more drastic fluctuations than the average fluctuation in the total structure, then, undertaking preferential rearrangements under the thermomechanical stimulus. In the framework of a quasi-point defects (QPDs) model, the activation of the β relaxation is a non-elastic shear strain component and is regarded as the minimum unit of deformation [32]. The macroscopic strain γ_β induced by the β relaxation event is accumulated by a strain rate upon the β relaxation timescale [33]

$$\dot{\gamma}_\beta^\infty - \dot{\gamma}_\beta = \dot{\gamma}_\beta \tau_\beta \quad (7)$$

where γ_β^∞ is the characteristic strain value, which is described as

$$\gamma_\beta^\infty = \sigma_\alpha \Delta J_\beta = \sigma_\alpha (J_{\beta_r} - J_{\beta_u}) \quad (8)$$

where the ΔJ_β is the variation of the compliance before and after β relaxation, σ_α is the characteristic activation stress, J_{β_r} is the compliance at the beginning of the β relaxation process and J_{β_u} is that at the end.

Here, we continue with the distribution thinking of our previous work to correlate the β relaxation time to the heterogenous defect sites of MG, which is inherently controlled by the distribution of the activation energy. Then, a distribution of the relaxation times is described from the perspective of thermodynamic considerations by a mathematical method called discrete normalized Gumbel distribution [33]

$$w_\beta^i = \frac{\exp\left\{B_\beta \ln\left(\frac{\tau_i}{\bar{\tau}}\right) - \exp\left[B_\beta \ln\left(\frac{\tau_i}{\bar{\tau}}\right)\right]\right\}}{\sum_i \exp\left\{B_\beta \ln\left(\frac{\tau_i}{\bar{\tau}}\right) - \exp\left[B_\beta \ln\left(\frac{\tau_i}{\bar{\tau}}\right)\right]\right\}} \quad (9)$$

where w_β^i is the probability weight of the i -type unit of β relaxation, τ_i is the corresponding characteristic relaxation time, B_β is the distribution factor ranging from 0 to 1, and $\bar{\tau}$ is the average characteristic relaxation time. The β relaxation time obtained by DMA is an average time, lacking the distribution. Each of the isolated relaxation units gives a particular kinetic process and converges into a total β relaxation event. In other words, the sum of the individual strain rate of these isolated relaxation units is the final macroscopic strain rate. In consideration of the distribution of isolated relaxation units, the average relaxation time is equivalently substituted by the discrete normalized Gumbel distribution of the β relaxation times. Consequently, Eq. (7) can be rewritten as

$$\sum_{i=1}^n \frac{w_\beta^i \dot{\gamma}_\beta^\infty - \dot{\gamma}_\beta^i}{\tau_\beta^i} = \dot{\gamma}_\beta \quad (10)$$

To describe the evolution of the general compliance J_β tailored by the β relaxation process, Eq. (10) was integrated to give an addition of all contributions from these relaxation units as

$$J_\beta = (J_{\beta_r} - J_{\beta_u}) \sum_{i=1}^n w_\beta^i \left[1 - \exp\left(\frac{-t}{\tau_\beta^i}\right) \right] \quad (11)$$

Then, a Laplace transform displays the evolution of the compliance on driving frequency of MGs as

$$J_\beta^*(\omega) = J_\beta \sum_{i=1}^n \frac{w_\beta^i}{1 + i\omega\tau_\beta^i} = J_\beta'(\omega) + iJ_\beta''(\omega) \quad (12)$$

where $J_\beta'(\omega)$ and $J_\beta''(\omega)$ are the storage compliance and loss compliance correlated to the β relaxation, respectively.

Fig. 1(a) shows the calculated evolution of the normalized loss modulus E''/E_u on the temperature at training frequency ranging from 10^{-3} to 10^2 Hz. The loss modulus E'' at ambient temperature is negligibly dependent on the frequency. The homogeneous viscous flow was recently obtained by ultrasonic agitation at a high frequency of 20,000 Hz, which increases the relaxation enthalpy from 0.11 to 0.26 kJ mol $^{-1}$ [34]. However, such a high frequency even induces partial crystallization in a Zr-Cu-Fe-Al MG [20]. Interestingly, La $_{30}$ Ce $_{30}$ Ni $_{10}$ Al $_{20}$ Co $_{10}$ MG displays considerable atomic mobility around the β relaxation peak temperature, providing an unexpected possibility to rejuvenate MGs at a relatively low frequency and at the same time to avoid crystallization behavior. Then we would like to emphasize that the training in β relaxation requires the occurrence of the β relaxation peak rather than the detection of the entire β relaxation region. The peak temperature increases with the training frequency, while the peak intensity is independent of whether training frequency or temperature.

Based on the correlation between the normalized loss modulus E''/E_u and temperature, the input energy at any temperature ΔW_0 can be computed (as shown in Fig. 1(b)). At a given temperature, the ΔW_0 increases with the training frequency, though there is a non-monotonic evolution of the loss modulus. Higher driving frequency injects more mechanical energy into MGs though they look more like a solid in the situation of the high driving frequency. At a given frequency, there is a one-to-one relationship between the loss modulus and ΔW_0 . It is worth noting that whether the input energy promotes atomic rearrangements towards structural relaxation or rejuvenation depends on its quantity. Here we took the truly experimental training frequency, ranging from 0.01 to 10 Hz. To determine the training temperature region, the total input energy ΔW was accumulated by the sum of ΔW_0 upon the full temperature region (as shown in Fig. 1(c)). The total input energy ΔW increases with an increase in the training frequency and temperature. Here a group of terminal temperatures was chosen as 323, 343, 363, and 383 K, respectively. An empirical exponential fit was used to describe the correlation between the total input energy ΔW and the training frequency at various terminal temperatures. As shown in Fig. 1(d), a good fitting can be observed, and the exponential factor increases from 0.84 to 1.00 when the terminal temperature increases from 323 to 383 K. In other words, a more apparent difference in total input energy ΔW can be obtained at the terminal temperature of 383 K, which is more beneficial to explore the effect of training frequency on rejuvenating MGs.

Fig. 2 shows a series of technical protocols. The samples were heated to 383 K at a heating rate of 3 K min $^{-1}$ and training frequencies of 0.01, 0.1, 1, and 10 Hz (termed as S1, S2, S3, and S4), then cooled to room temperature. The effect of the input mechanical energy on the energetic state of MGs was investigated by the DSC measurement. Fig. 3 shows the heat flow difference between the as-cast glass and sample S4 and their corresponding crystallized state as a reference. After training β relaxation with 10 Hz, the exothermic heat of relaxation ΔH increases from 0.34 to 0.49 kJ mol $^{-1}$. We note that this stored energy is in quantitative agreement with that obtained by the elastostatics loading [35]. The quantity falls well into the cold-rolled monolithic MGs (~ 0.3 – 1.8 kJ mol $^{-1}$ [11]). The present work demonstrates that training in β relaxation process is a kind of elegant and convenient strategy to rejuvenate MGs.

Notably, the increase of the relaxation enthalpy is essentially a mean-field parameter, in which the information on structural/dynamic heterogeneity is absent. The evolution of the structural heterogeneity could be explored from the perspective of atomic mobility and the distribution of relaxation units. The results of the mechanical relaxation spectrum performed after activating

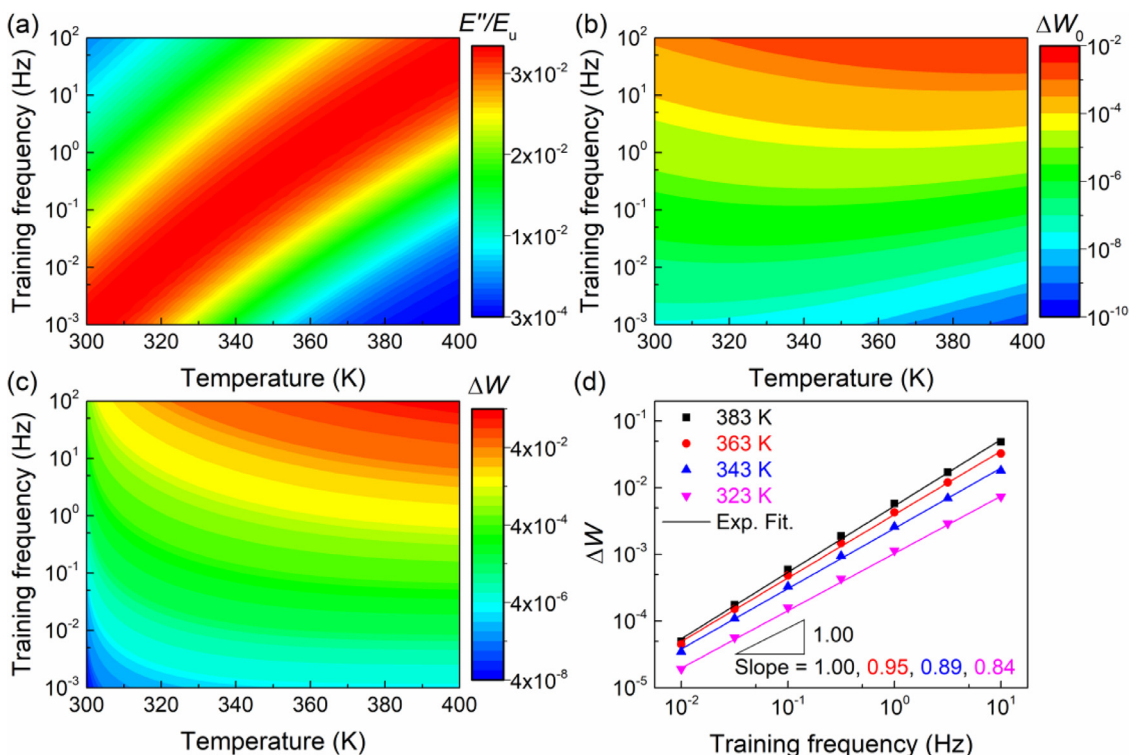


Fig. 1. Spectrum of the β relaxation training. Calculation of the evolution of (a) the normalized loss modulus, (b) ΔW ; (c) the sum W with the temperature at training frequencies ranging from 10^{-3} to 10^2 Hz. The parameter of calculation is from Ref. [1]; (d) Evolution of the sum W with training frequency at a temperature ranging from 323 to 383 K.

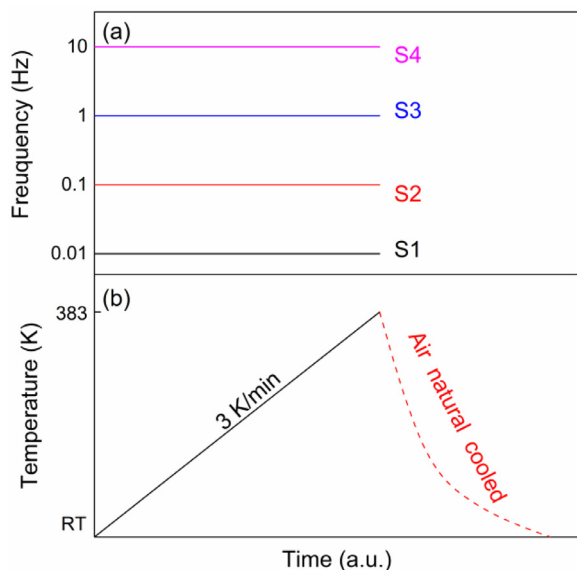


Fig. 2. Schematic illustration of the (a) training frequency and (b) temperature. The samples with a training frequency of 0.01, 0.1, 1, and 10 Hz are termed S1, S2, S3, and S4, respectively.

β relaxation are displayed in Fig. 4(a). Two main mechanical relaxation processes, i.e., the β relaxation and α relaxation process, are observed. Evidently, the intensity of the β and α relaxation processes increases with the training frequency. The enhancement of the mechanical relaxations indicates that the current atomic mobility is in direct proportion to the training frequency. For a more intuitive view, the evolution of the peak temperature of the mechanical relaxations is shown in Fig. 4(b). The peak temperature of

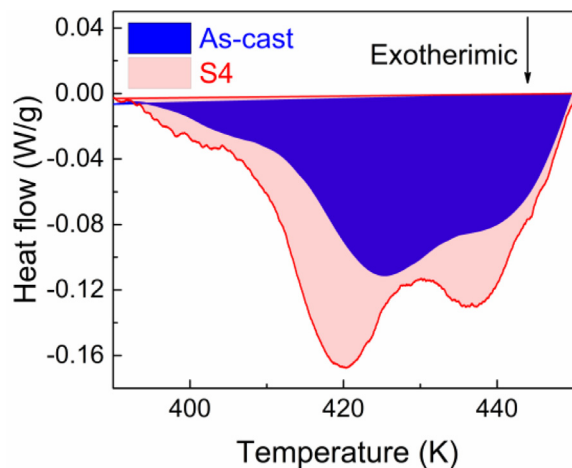


Fig. 3. DSC curves of the as-cast and trained sample via β relaxation with 10 Hz.

the α relaxation is negligibly dependent on the training frequency ($\Delta T \sim 0.3$ K) while that of β relaxation progressively decreases from 368 to 364 K with the pre-activation frequency. The evolution of mechanical relaxations is attributed to the increase in the training frequency, where the input mechanical energy plays a crucial role.

In the case of the DMA measurement, it has been reported that the rejuvenation by cold-rolling significantly enhances the “excess wing” of β relaxation [36]. However, this mechanical history was erased by the high atomic mobility, while the α relaxation process is not sensitive to the cold-rolling treatment. Undergoing the rejuvenation by cryogenic thermal cycling, the α relaxation peak temperature is lowered by 2.3 K, but there is no clear change in the β relaxation process [8]. Recently, Zhang et al. [6] reported that the strength of the β relaxation process could be achieved by control-

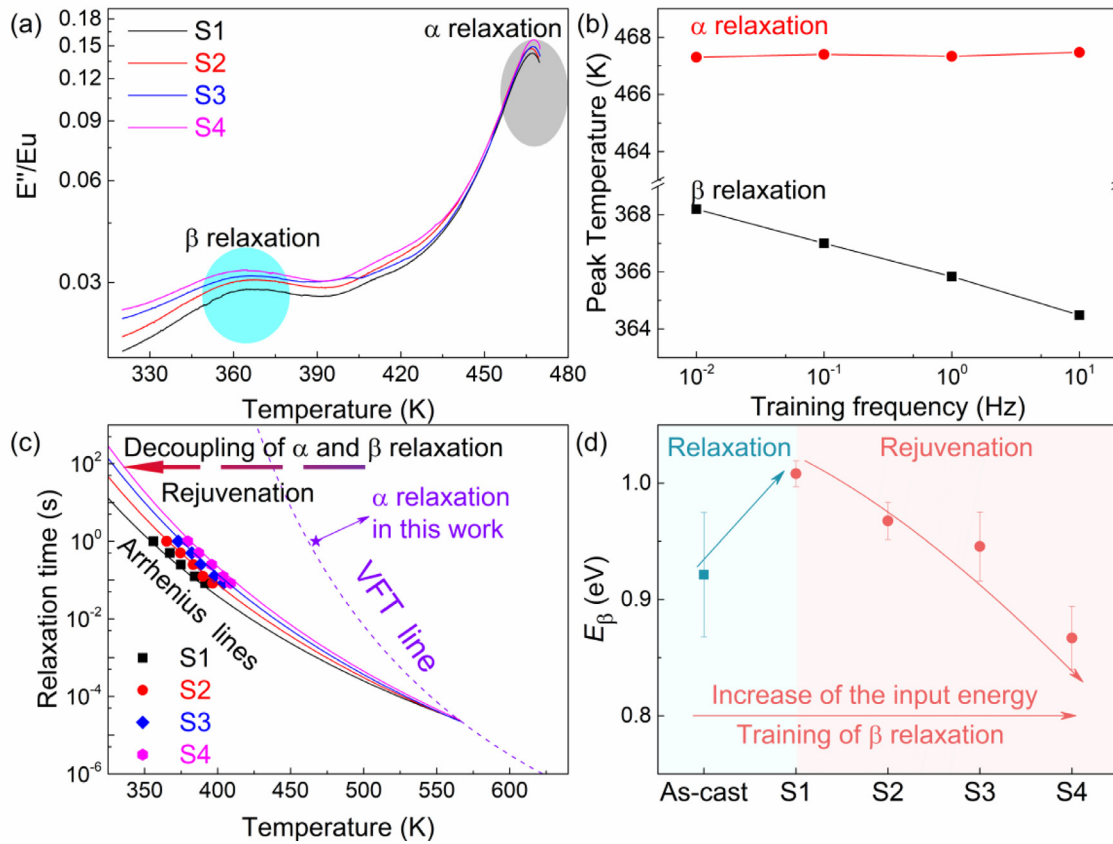


Fig. 4. (a) Evolution of the normalized loss modulus E''/E_u with temperature of the samples S1, S2, S3, and S4, respectively. (b) Evolution of peak temperature of β relaxation and α relaxation at different training frequencies; (c) Evolution of β relaxation time with temperature for samples S1, S2, S3, and S4, respectively. The solid lines represent fits by Eq. (13). The dash line was computed from [41]; (d) Evolution of the activation energy of the β relaxation, E_β , with variation in training frequency. The activation energy of as-cast glass is from [41].

ling the mechanical cycling, although no further information about α relaxation was given in the previous investigation. In this study, however, we proved the feasibility of training in the mechanical relaxation mode to rejuvenate MGs. Additionally, the training of β relaxation in this work is more effective to modulate the β - and α - relaxations than those reported in the literature.

The evolution of the mechanical relaxations on driving frequencies was performed to study the effect of training β relaxation on the microstructural heterogeneity. An empirical Arrhenius equation to describe the correlation between the frequency and peak temperature of the β relaxation T_β [37]:

$$f = f_0 \exp(-E_\beta/k_B T_\beta) \quad (13)$$

where f is the driving frequency, f_0 is a pre-parameter, E_β is the β relaxation activation energy, and k_B is the Boltzmann constant. The correlation between the characteristic relaxation time of the β relaxation and temperature and the corresponding fitting results by Eq. (13) at various training frequencies are shown in Fig. 4(c). The relaxation time shifts to a lower temperature with increasing training frequency. The response of an inherent heterogeneous microstructure of MGs to applied stimulations is the variation in the relaxation time of the local regions, i.e., these loosely packed regions possess faster relaxation dynamics while those densely packed regions usually correspond to slower relaxation dynamics. In consideration of the negligible change in α relaxation time, it is reasonable to conclude that the loosely packed regions with faster relaxation times are proliferated and thus take the most vital role in the control of mechanical relaxations. As for the densely packed regions, the training of β relaxation only introduces an enhancement of their mobility and intensity. In fact, structural re-

laxation and rejuvenation are connected by a two-way channel. Here we would like to emphasize that the structural relaxation is spontaneous, but the rejuvenation is contrived and coercive accomplished. As reported by Greer et al. [38], rejuvenation involves at least two different processes or even multiple processes. Based on this investigation, it is highly likely that in our work, the rejuvenation shows an apparently different effect on activation of the loosely packed regions (associated with β relaxation) and the densely packed regions (related to α relaxation).

Previous investigations [39,40] have demonstrated the decoupling behavior of the mechanical relaxations in glass-forming liquids and ignored the possible effects of structural state. Indeed, the finding of the relaxation decoupling possesses the significance of a milestone and provides further clarification of the glassy dynamics. The Vogel–Fulcher–Tammann (VFT) equation, with parameters $B = 5907$ K and $T_0 = 278$ K from mechanical spectroscopy measurements in ref. [41], can describe reasonably well the temperature dependence of the α relaxation time measured in this work (Fig. 4(c)). One can see that the mechanical relaxations split into α - and β - relaxations at a crossover temperature in a moderately supercooled range as temperature decreases. Our results suggest that structural rejuvenation elevates the decoupling degree of α - and β - relaxations. In addition, the evolution of β relaxation activation energy E_β on the training frequency was analyzed in detail and compared with that of the as-cast sample (as shown in Fig. 4(d)). Compared with the as-cast sample, an increase in E_β was observed as the training frequency is relatively low, but an enhancement of that was shown in sample S4. The crossover from the decrease to increase of the loss modulus with the increase in training frequency confirms the threshold of the dynamic com-

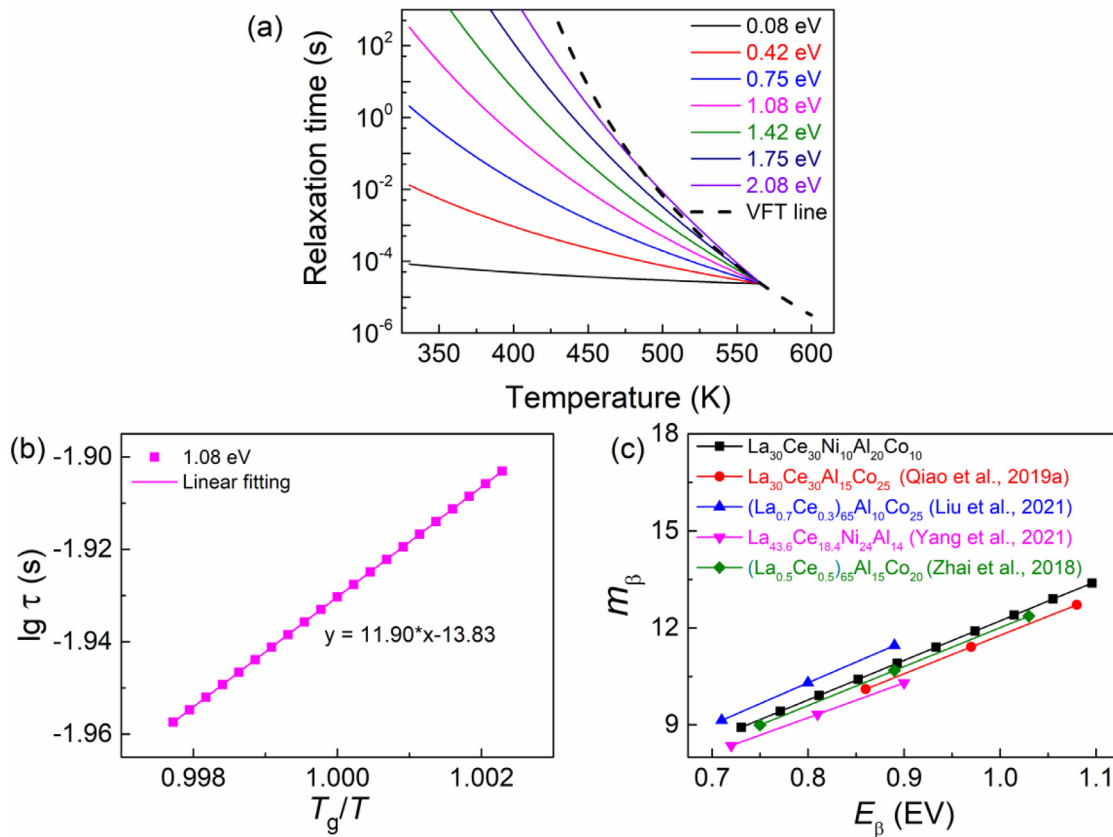


Fig. 5. (a) Change in the evolution of the β relaxation time versus temperature with activation energy E_β ranging from 0.08 to 2.08 eV. The dash line is the VFT line. (b) Linear fitting between the logarithm of β relaxation time and the reciprocal temperature. The slope is equal to the secondary fragility m_β . (c) Evolution of the secondary fragility m_β with activation energy E_β in typical MG systems. Experimental data of other MGs are from previous references [43–46].

petition between structural relaxation and rejuvenation in such a thermal-mechanical cyclic loading. The change of the β relaxation activation energy stands for the change in the glass state, which is tailored by the training process; it gets positive in the case of rejuvenation and falls below zero if relaxation occurs. Under the stimulation of constant driving frequency and heating rate, it characterizes the degree of difficulty to thermally activate the local atomic rearrangements. Here structural relaxation can be regarded as the frozen of defects while rejuvenation is corresponding to the activation of that. When the training frequency is relatively low (such as 0.01 Hz), there is a net frozen rate of flow units which is characterized by the increment of the β -relaxation activation energy. With the increase in training frequency, the level of rejuvenation was improved and ultimately surpasses the degree of structural relaxation.

As we showed in Fig. 4(c), the effect of structural relaxation and rejuvenation on the β relaxation have been erased at the crossover temperature. Based on Eq. (13), the evolution of the β relaxation time on the temperature at various energetic states can be deduced from

$$\begin{cases} \tau_\beta = \tau_0 \exp(-E_\beta/k_B T) \\ \tau(T = 566.67 \text{ K}) = 5 \cdot 10^{-4} \text{ s} \end{cases} \quad (14)$$

Here E_β is the crucial index to level the energetic state of MGs. Further calculations of a cluster of τ_β - T curves are displayed in Fig. 5(a), spanning the E_β range from 0.08 to 2.08 eV. We can speculate the theoretical maximum degree of rejuvenation in MGs is corresponding to the lowest value of $E_\beta \approx 0$ eV, while the maximum degree of structural relaxation is correlated to the highest value of $E_\beta \approx E_\alpha$, in the latter case the β relaxation time almost

coincides with that of α relaxation. To the best of our knowledge, there is no work about the mechanical relaxation dynamics in the ultimately rejuvenated or ultrastable MGs has been reported. Thus, verification of the maximum degree of rejuvenation and structural relaxation is difficult but fascinating. Maybe MD simulations and the exploration of ultrastable glass could be helpful to further work. A necessary issue is the exploration of the correlation between the evolution of the β relaxation time controlled by the activation energy and mechanical properties of MGs. The fragility relates to the decay rate of the relaxation dynamics of glass-forming liquids at T_g , which is readily computed as [42]

$$m = \frac{d \log \tau_\alpha}{d(T_g/T)} \quad (15)$$

In this connection, the glasses with a small value of m are categorized as strong systems, while a larger value of the fragility parameter is regarded as fragile glass. It should be mentioned that the fragility m can be determined directly by the dependence of τ_α on temperature and keeps constant at a given pressure. In other words, the fragility value computed by the α relaxation time is independent of the energetic state of MGs.

It has been accepted that β relaxation is the precursor of α relaxation [21], indicating the common characteristics of mechanical relaxations. To describe the correlation between mechanical relaxation time and the properties of MGs in a quantitative manner, a secondary fragility m_β is defined to describe the decay rate of the β relaxation time at T_g as

$$m_\beta = \frac{d \log \tau_\beta}{d(T_g/T)} \quad (16)$$

Taking $E_\beta = 1.08$ eV for example, the corresponding computation process is shown in Fig. 5(b). An apparent linear correlation between the logarithm of τ_β and the reciprocal temperature can be observed. The slope is equal to the value of m_β . Then, the evolution of the secondary fragility m_β on the β relaxation activation energy was determined and shown in Fig. 5(c). The experimental results of other MGs were also obtained from the literature [43–46]. The secondary fragility values are about 8–14, which is significantly lower than that computed for the α relaxation time because of the relatively slower decay rate of the β relaxation time. We found that m_β is intriguingly linear with the β relaxation activation energy. The traditional fragility m is known to be insensitive to a series of external variables and is considered an intrinsic property of the glass-forming liquids. Undoubtedly, the concept of secondary fragility m_β is more abundant than that of the traditional fragility m . The decrease in the secondary fragility m_β with the expanded degree of structural rejuvenation, or decreasing the β relaxation activation energy, provides a plausible explanation for the enhancement of plasticity of MGs by rejuvenation. Furthermore, the exploration of the correlation between the secondary fragility m_β and the plasticity in ultimately rejuvenated MGs would be interesting.

The inherent microstructural heterogeneity of MGs gives abundant possibilities to modulate their mechanical/physical properties, especially the deformation process. The dynamic heterogeneity naturally originates from the individual activation of flow units with a wide range of relaxation times and their interaction. From the perspective of the hierarchical flow defects [32], the anelastic strain ε_{an} and the viscoplastic strain ε_{vp} are corresponding to the appearance of shear microdomains and their mergence, which are composed by the elementary units of the deformation process, i.e., the activation of the β relaxation. The shear microdomain looks more like an intelligent spring, which can store the reversible energy at a limited timescale (anelastic component) but crack and cancel those anelastic energies at a longer timescale (viscoplastic component). Noted that Eq. (13) only considers the thermal contribution to the activation of β relaxation, while ignoring the mechanical work. With the assistance of the mechanical work, the complete Arrhenius equation can be rewritten as

$$\tau = \tau_0 \exp \left[\frac{E_\beta \left(1 - \frac{\sigma_a}{\sigma_0}\right)^{\frac{2}{3}}}{k_B T} \right] \quad (17)$$

where σ_0 is the stress value which vanishes the energy barriers at 0 K, σ_a is the applied shear stress.

Taking the β relaxation movements as the elementary units, the corresponding hierarchical movements are described by a specific correlation factor χ . Here, the correlation factor χ ($0 \leq \chi \leq 1$) is closely correlated with the QPD concentration [32]. $\chi = 0$ is regarded as the ideal crystal without any structural defect, i.e., a fully ordered structure. Especially, the movement of each relaxation unit is totally dependent on others and possesses active interatomic and enthalpic interactions. On the contrary, $\chi = 1$ is regarded as the ideal gas, a fully disordered structure. Then the movement of each relaxation unit is totally independent of others and no interaction occurs. For MG systems, the existence of the hierarchical correlation among these relaxation units indicates more complex movements require longer relaxation time to involve. Thus, it is necessary to define an elementary timescale τ_{mol} that from the start of a completed elementary event to the end of annihilation of the corresponding sheared microdomains, that is [33]

$$\tau_{mol} = \tau_0 \left(\frac{\tau_\beta}{\tau_0} \right)^{\frac{1}{\chi}} \quad (18)$$

where τ_0 is the timescale parameter. In consideration of the specificity of the i -th elementary relaxation unit in Eq. (10), Eq. (15) is

discretized as

$$\tau_{moli} = \tau_0 \left(\frac{\tau_{\beta_i}}{\tau_0} \right)^{\frac{1}{\chi}} \quad (19)$$

where τ_{moli} and τ_{β_i} are the elementary timescale and characteristic relaxation time of the i -th relaxation unit. Based on Eq. (16), the elementary timescale shows a strong dependence on the value of the correlation factor χ or the degree of structural order. The evolution of the characteristic time for the anelastic deformation τ_{an} on the structural order values evolves following [33]

$$\tau_{an} = \tau_{mol} \chi^{\frac{1}{\chi}} \quad (20)$$

For polymer and MG systems, the correlation factor χ is a vital parameter that connects to the microstructural heterogeneity [31]. When the temperature is below the glass transition temperature T_g , it has been accepted that MGs keep an iso-configurational state (also called “frozen” state) ignoring the effect of physical aging, rejuvenation, and external mechanical stimulus, which is characterized by a constant value of the correlation factor χ .

As we mentioned above, the anelastic component is closely correlated with the formation of shear microdomains. The structural disorder is directly connected to these anelastic components. However, the viscoplastic strain is associated with the annihilation of shear microdomains, which brings about a more homogenous structure. The real degree of structural order can be described as

$$\begin{cases} (T, \gamma) = (T_g) + A_{an} \gamma_{an} - A_{vp} \gamma_{vp}, & T < T_g \\ (T) = (T_g) + \chi_0 (T - T_g) + A_{an} \gamma_{an} - A_{vp} \gamma_{vp}, & T \geq T_g \end{cases} \quad (21)$$

where χ_0 is the rate parameter which depends on the material attribute. Similar to the β relaxation component, the anelastic component γ_{an} should also follow an individual Gumbel distribution and is accumulated by a series of anelastic atomic rearrangements as

$$\begin{cases} \dot{\gamma}_{an} = \sum_{i=1}^n \frac{(w_{an}^i \gamma_{an}^\infty) - \gamma_{an}^i}{\tau_{an}^i} \\ w_{an}^i = \frac{\exp \left\{ B_{an} \ln \left(\frac{\tau_{an}^i}{\tau_{an}^\infty} \right) - \exp \left[B_{an} \ln \left(\frac{\tau_{an}^i}{\tau_{an}^\infty} \right) \right] \right\}}{\sum_i \exp \left\{ B_{an} \ln \left(\frac{\tau_{an}^i}{\tau_{an}^\infty} \right) - \exp \left[B_{an} \ln \left(\frac{\tau_{an}^i}{\tau_{an}^\infty} \right) \right] \right\}} \end{cases} \quad (22)$$

where w_{an}^i , γ_{an}^i , and τ_{an}^i are the probability weight, anelastic strain rate, and anelastic relaxation time of the i -type anelastic relaxation unit, respectively. γ_{an}^∞ is the equilibrium strain for the anelastic component and can be obtained by the anelastic process as [33]

$$\gamma_{an}^\infty = \sigma_\alpha \Delta J_{an} \quad (23)$$

where ΔJ_{an} is the reversible part of the change of compliance induced by anelastic processes. The anelastic and viscoplastic component are corresponding to the wane and wax of shear microdomains, therefore, the viscoplastic strain rate can be computed as

$$\dot{\gamma}_{vp} = \frac{\sigma_\alpha \Delta J_{an}}{\tau_{mol}} \quad (24)$$

and

$$\begin{cases} \dot{\gamma}_{vp} = \sum_{i=1}^n \frac{(w_{vp}^i \gamma_{vp}^\infty) - \gamma_{vp}^i}{\tau_{vp}^i} \\ w_{vp}^i = \frac{\exp \left\{ B_{vp} \ln \left(\frac{\tau_{vp}^i}{\tau_{vp}^\infty} \right) - \exp \left[B_{vp} \ln \left(\frac{\tau_{vp}^i}{\tau_{vp}^\infty} \right) \right] \right\}}{\sum_i \exp \left\{ B_{vp} \ln \left(\frac{\tau_{vp}^i}{\tau_{vp}^\infty} \right) - \exp \left[B_{vp} \ln \left(\frac{\tau_{vp}^i}{\tau_{vp}^\infty} \right) \right] \right\}} \end{cases} \quad (25)$$

where w_{vp}^i , γ_{vp}^i , and τ_{vp}^i are the probability weight, viscoplastic strain rate, and viscoplastic relaxation time of the i -type viscoplastic relaxation unit, respectively. γ_{vp}^∞ is the equilibrium strain for the viscoplastic component and can be obtained by the viscoplastic process as

$$\gamma_{vp}^\infty = \sigma_\alpha \Delta J_{vp} \quad (26)$$

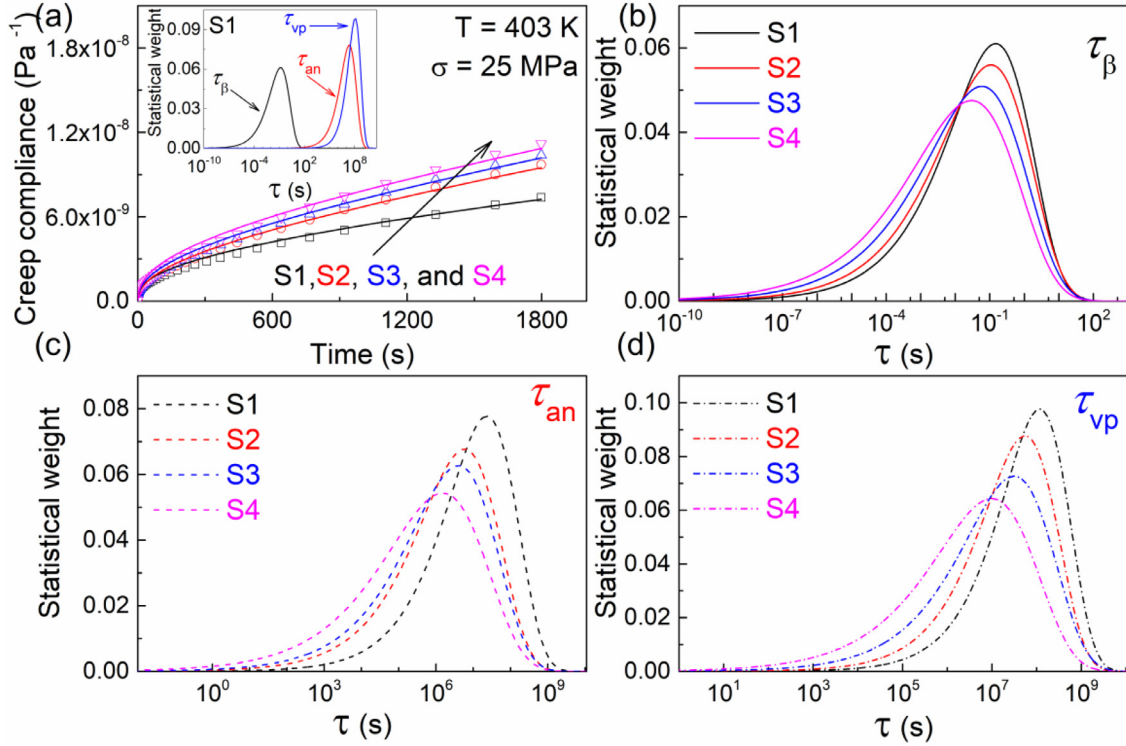


Fig. 6. (a) Creep strain of the sample at temperature 403 K and stress 25 MPa. The solid lines were fitted by Eq. (26). Inset shows the distribution of the characteristic relaxation time of the β relaxation, anelastic, and viscoplastic components of sample S1 at 403 K; Evolution of the calculated distribution of the characteristic relaxation time of (b) the β relaxation, (c) the anelastic, and (d) viscoplastic components of the samples S1, S2, S3 and S4, respectively.

and

$$\Delta J_{vp} = (J_{\alpha_r} - J_{\alpha_u}) - \Delta J_{an} \quad (27)$$

where J_{α_r} and J_{α_u} are the compliances at the beginning and end of the α relaxation process.

In a nominal linearly elastic region, the effect of stress on the modulus, compliance, and relaxation time could be neglected. The evolution of modulus/compliance in the temperature/time domain can be described by the sum of contributions of β relaxation events, anelastic and viscoplastic components, i.e., the sum of explicit integration of Eqs. (10), (22), and (26). The general expression is obtained as

$$\begin{aligned} J(t) = & J_{el} + \Delta J_{\beta} \sum_{i=1}^n w_{\beta}^i \left[1 - \exp\left(\frac{-t}{\tau_{\beta}^i}\right) \right] \\ & + \Delta J_{an} \sum_{i=1}^n w_{an}^i \left[1 - \exp\left(\frac{-t}{\tau_{an}^i}\right) \right] \\ & + \Delta J_{vp} \sum_{i=1}^n w_{vp}^i \left[1 - \exp\left(\frac{-t}{\tau_{vp}^i}\right) \right] \end{aligned} \quad (28)$$

To clarify the effect of training of β relaxation on the mechanical relaxation component, anelastic component, and viscoplastic component, a group of tensile creep measurements was proposed. A group of creep tests of samples with different training frequencies was carried out at a temperature of 403 K and a stress of 25 MPa (as shown in Fig. 6(a)). The instantaneous response was subtracted from the total strain. Apparently, an increase in strain and a decrease in strain rate with time can be observed. The phenomenological steady-state strain rate, a vital parameter to systematically study the time-dependent deformation behavior of viscoelastic materials, increases with the applied temperature. At the first sight, increasing the training frequency or activating the β relaxation is beneficial to promote the creep process, characterized

by the enhancement of the creep strain and the improvement of the steady-state strain rate. According to the results of Lei et al. [15], the overall creep strain gets suppressed with expanding aging time (raising the level of structural relaxation) but is not noticeably affected by structural rejuvenation induced by cryogenic cycling. Compared with our results, it can also be regarded as the peculiarity of the rejuvenation strategy of training β relaxation.

On the other hand, it is necessary to clarify whether the training of β relaxation has a significant effect on the evolution of the relaxation time spectrum of creep. In Eq. (28), there are a series of parameters devoted to the characterization of the β relaxation, anelastic, and viscoplastic components. The unrelaxed and relaxed modulus (J_{β_u} , J_{β_r} , J_{α_u} , and J_{α_r}) are directly read on the storage modulus versus temperature curve. The distribution parameters B_{β} , B_{an} , and B_{vp} are reached from the fit of the compliance versus time curve. Taking the creep result of sample S1 as an example, we calculated the three main components (the response of faster mechanical relaxations is integrated into the elastic component) of relaxation-time spectra, as shown in the inset of Fig. 6(a). There are three distinct peaks with various intensities and distributions which are corresponding to the β relaxation, anelastic, and viscoplastic components, respectively. The deformation induced by the β relaxation component shows the widest and faster distribution, while that of the viscoplastic component is the longest and narrowest. We note that the distribution of the β relaxation component has ignorable interaction with other components, while the anelastic component has an apparent interaction with the viscoplastic component. There is no doubt that the β relaxation event plays as an elementary unit to undertake the external mechanical stress, regardless of whether the anelastic or viscoplastic components originate from the activation of a group of β relaxation events. This picture also gives a scene about how the dynamical heterogeneities evolve. Cao et al. [47] reported a crossover from shear deformation creep to diffusional creep with loading time in

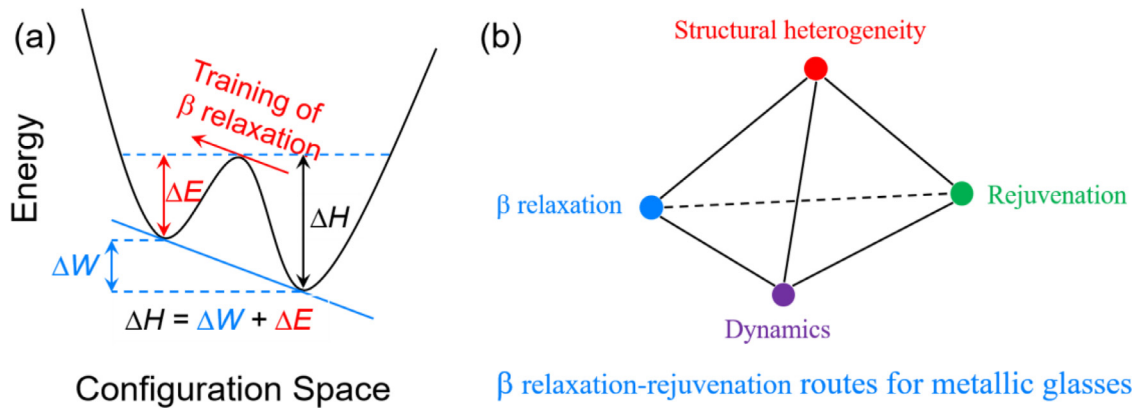


Fig. 7. (a) Scheme of the physical mechanism of rejuvenation by training β relaxation. (b) Summary of the routes among the structural heterogeneity, β relaxation, structural rejuvenation, and dynamics in MGs.

Table 1

The fitting parameters B_β , B_{an} , B_{vp} , $\bar{\tau}_\beta$, $\bar{\tau}_{an}$, and $\bar{\tau}_{vp}$ for creep of the La-based MG using the QPD model.

Sample	B_β	B_{an}	B_{vp}	$\bar{\tau}_\beta$ (s)	$\bar{\tau}_{an}$ (s)	$\bar{\tau}_{vp}$ (s)	$\bar{\tau}_{vp}/\bar{\tau}_\beta$	$\bar{\tau}_{an}/\bar{\tau}_\beta$	$\bar{\tau}_{vp}/\bar{\tau}_{an}$
S1	0.36	0.46	0.58	0.15	2.34×10^7	2.19×10^8	1.46×10^9	1.56×10^8	9.24
S2	0.33	0.40	0.52	0.11	5.90×10^6	5.58×10^7	5.07×10^8	5.36×10^7	9.45
S3	0.30	0.37	0.43	0.08	4.05×10^6	3.19×10^7	4.14×10^8	5.25×10^7	7.88
S4	0.28	0.32	0.38	0.03	1.53×10^6	1.01×10^7	3.37×10^8	5.10×10^7	6.60

a model MG. It is highly likely that in this work, the mechanism is a complex process, i.e., the transition from the anelastic process to the viscoplastic process. The distribution of these processes provides plenty of information about the relaxation time and heterogeneity.

The following discussion addresses the details of the effect of training β relaxation on the distribution of relaxation times, as resolved by their size/time constant. Fig. 6(b–d) show the evolution of relaxation time distribution of β relaxation, anelastic, and viscoplastic components at different training frequency. The fitting values of B_β , B_{an} , B_{vp} , $\bar{\tau}_\beta$, $\bar{\tau}_{an}$, and $\bar{\tau}_{vp}$, are listed in Table 1. Mathematically, the distribution parameter characterizes the distribution width of relaxation times, and the relaxation time average indicates the dynamic rate. Here, the values of relaxation time average are corresponding to the level of energetic state while the distribution factor is correlated to the degree of dynamic heterogeneity of MGs. The flow defects or flow units are those loosely packed microregions with faster relaxation time and more active dynamics. Consequently, we can give the distribution factor clearer significance that it is inherently correlated to the structural configuration of MGs. Several points can be obtained by comparing these fitting parameters in different training frequencies: (i) By increasing the training frequency, a universal significant decrease of distribution factor can be observed, accompanying the decrease of the characteristic relaxation times. This result indicates that training β relaxation more frequently is beneficial to enhance the size or number of loosely packed regions. A wider distribution of relaxation time with upping the level of rejuvenation stands for the activation of more types of flow defects in the deformation process, which is similar to the results of mechanical relaxations and nanoindentation [6]; (ii) The ratio $\bar{\tau}_{an}/\bar{\tau}_\beta$ and $\bar{\tau}_{vp}/\bar{\tau}_\beta$ decrease with the training frequency, which indicates rejuvenation improves effectively the hierarchical deformation. Additionally, the decrease in the value of $\bar{\tau}_{vp}/\bar{\tau}_{an}$ demonstrates that anelastic deformation takes a more vital role in rejuvenation dynamics.

For the as-cast MGs, the loosely packed regions have indeed high atomic mobility and vice versa. The differences between adjacent regions induce variations of the modulus from one location

to its neighbors on the microscopic structure. It can be expected that upon frequent training, all the regions are asked to adjust themselves to follow a forced relaxation path to adapt to external stress. Our results show that modulation of energy states of MGs can be achieved by involving higher training frequency within a certain range of training temperature because it promotes the MG to remember more of its previous mechanical history. Consequently, a scheme of the physical mechanism of rejuvenation by training β relaxation can be constructed, i.e., the storage of mechanical history upon the training process lowers the activation barrier of atomic rearrangements (as shown in Fig. 7(a)). On the other hand, one can expect that training of the β relaxation at an accurate temperature/frequency region can introduce more defects and a higher degree of heterogeneity as the β relaxation is related to the activation of structural heterogeneity. Obviously, the structural heterogeneity is the core that connects the β relaxation and rejuvenation, and then evolves plenty of dynamics. The rejuvenation of MGs indeed strengthens mechanical relaxations, while training in β relaxation also provides flexibility to rejuvenation. Finally, a group of routes that give the correlation between structural heterogeneity, β relaxation, rejuvenation, and dynamics of MGs are summarized in Fig. 7(b). Innovative design and processing of MGs through training β relaxation, with inherent structures tuned to facilitate rejuvenation, offer possibilities in expanding the ductility and workability.

4. Conclusions

The aim of the current paper is to advance understanding of the effect of training the β relaxation on the structural and dynamic properties of MGs, and especially how MGs can be rejuvenated. Firstly, we have explored the applicable technological parameters in the framework of the QPD model. Concentrating on rejuvenation, atomic mobility increases with the training frequency. Decoupling of the β relaxation and α relaxation can be observed as the structural heterogeneity increases. Rejuvenated MGs show lower activation energy and a lower peak temperature of the β relaxation, and a reduced value of the secondary fragility m_β . Focusing on dynamics, increasing training frequency accelerates the β

relaxation, anelastic, and viscoplastic components of deformation and expands their distribution.

In the current work, we only presented the training frequency at the constant temperature region to achieve the rejuvenation of MGs. The current findings will encourage future efforts in exploring the signatures of rejuvenation of MGs under some other stimuli, such as temperature region, heating rate, sample size, and faster mechanical relaxation modes. It can be predicted that training in mechanical relaxation can drive MGs to reside at any energetic state between ultimately rejuvenated and ultrastable MGs in the potential energy landscape.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work is supported by the NSFC (Grant Nos. 51971178 and 52271153), the Natural Science Basic Research Plan for Distinguished Young Scholars in Shaanxi Province (Grant No. 2021JC-12), Fundamental Research Funds for the Central Universities (Grant No. D5000220034) and the Natural Science Foundation of Chongqing (Grant No. cstc2020jcyj-jqX0001). YJW was financially supported by NSFC (Grant No. 12072344) and the Youth Innovation Promotion Association of the Chinese Academy of Sciences. YY acknowledges financial support from Research Grant Council (RGC), and the Hong Kong government through the General Research Fund (GRF) with Grant Nos. CityU11200719 and CityU11213118.

References

- [1] W.H. Wang, *Prog. Mater. Sci.* 106 (2019) 100561.
- [2] J.C. Qiao, Q. Wang, J.M. Pelletier, H. Kato, R. Casalini, D. Crespo, E. Pineda, Y. Yao, Y. Yang, *Prog. Mater. Sci.* 104 (2019) 250–329.
- [3] Y.J. Duan, L.T. Zhang, J.C. Qiao, Y.-J. Wang, Y. Yang, T. Wada, H. Kato, J.M. Pelletier, E. Pineda, D. Crespo, *Phys. Rev. Lett.* 129 (2022) 175501.
- [4] J.C. Qiao, L.T. Zhang, Y. Tong, G.J. Lyu, Q. Hao, K. Tao, *Adv. Mechan.* 52 (2022) 117–152.
- [5] T. Egami, *Ann. N.Y. Acad. Sci.* 371 (1981) 238–251.
- [6] L.T. Zhang, Y.J. Wang, E. Pineda, Y. Yang, J.C. Qiao, *Int. J. Plast.* 157 (2022) 103402.
- [7] J. Pan, Y.X. Wang, Q. Guo, D. Zhang, A.L. Greer, Y. Li, *Nat. Commun.* 9 (2018) 560.
- [8] S.V. Ketov, Y.H. Sun, S. Nachum, Z. Lu, A. Checchi, A.R. Beraldin, H.Y. Bai, W.H. Wang, D.V. Louzguine-Luzgin, M.A. Carpenter, A.L. Greer, *Nature* 524 (2015) 200–203.
- [9] W. Dmowski, Y. Yokoyama, A. Chuang, Y. Ren, M. Umemoto, K. Tsuchiya, A. Inoue, T. Egami, *Acta Mater.* 58 (2010) 429–438.
- [10] J. Pan, Y.P. Ivanov, W.H. Zhou, Y. Li, A.L. Greer, *Nature* 578 (2020) 559–562.
- [11] Y. Sun, A. Concustell, A.L. Greer, *Nat. Rev. Mater.* 1 (2016) 16039.
- [12] W. Guo, R. Yamada, J. Saida, *Intermetallics* 93 (2018) 141–147.
- [13] W. Guo, J. Saida, M. Zhao, S. Lü, S. Wu, *Mater. Sci. Eng. A* 759 (2019) 59–64.
- [14] W. Guo, J. Saida, M. Zhao, S. Lü, S. Wu, *Metall. Mater. Trans. A* 50 (2019) 1125–1129.
- [15] T.J. Lei, L.R. DaCosta, M. Liu, W.H. Wang, Y.H. Sun, A.L. Greer, M. Atzmon, *Acta Mater.* 164 (2019) 165–170.
- [16] A. Hassanpour, M. Vaidya, S.V. Divinski, G. Wilde, *Acta Mater.* 209 (2021) 116785.
- [17] B.S. Li, S. Xie, J.J. Kruzic, *Acta Mater.* 176 (2019) 278–288.
- [18] G.V. Afonin, O.A. Zamyatin, E.V. Zamyatina, V.A. Khonik, *Scr. Mater.* 186 (2020) 39–42.
- [19] S. Küchemann, C. Liu, E.M. Dufresne, J. Shin, R. Maaß, *Phys. Rev. B* 97 (2018) 014204.
- [20] D.V. Louzguine-Luzgin, M.Y. Zadorozhnyy, S.V. Ketov, J. Jiang, I.S. Golovin, A.S. Aronin, *Mater. Sci. Eng. A* 742 (2019) 526–531.
- [21] K.L. Ngai, Z. Wang, X.Q. Gao, H.B. Yu, W.H. Wang, *J. Chem. Phys.* 139 (2013) 014502.
- [22] K.L. Ngai, S. Capaccioli, *Phys. Rev. E* 69 (2004) 031501.
- [23] K. Ngai, *Relaxation and diffusion in complex systems*, Springer Science & Business Media, Switzerland, 2011.
- [24] T. Egami, S. Poon, Z. Zhang, V. Keppens, *Phys. Rev. B* 76 (2007) 024203.
- [25] X. Gong, X.-D. Wang, T. Xu, Q. Cao, D. Zhang, J.-Z. Jiang, *J. Phys. Chem. B* 125 (2021) 657–664.
- [26] S.Y. Di, H.B. Ke, Q.Q. Wang, J. Zhou, Y. Zhao, B.L. Shen, *Mater. Des.* 222 (2022) 111074.
- [27] H.B. Yu, X. Shen, Z. Wang, L. Gu, W.H. Wang, H.Y. Bai, *Phys. Rev. Lett.* 108 (2012) 015504.
- [28] X. Yuan, D. Şöpu, F. Spieckermann, K.K. Song, S.V. Ketov, K.G. Prashanth, J. Eckert, *Scr. Mater.* 212 (2022) 114575.
- [29] S. Li, P. Huang, F. Wang, *J. Alloys Compd.* 850 (2021) 156774.
- [30] W. Jiang, B. Zhang, *J. Appl. Phys.* 127 (2020) 115104.
- [31] J. Perez, *Solid State Ionics* 39 (1990) 69–79.
- [32] J. Perez, *Acta Metall.* 32 (1984) 2163–2173.
- [33] R. Rinaldi, R. Gaertner, L. Chazneau, C. Gauthier, *Int. J. Non-Linear Mech.* 46 (2011) 496–506.
- [34] X. Li, D. Wei, J.Y. Zhang, X.D. Liu, Z. Li, T.Y. Wang, Q.F. He, Y.J. Wang, J. Ma, W.H. Wang, Y. Yang, *Appl. Mater. Today* 21 (2020) 100866.
- [35] K.-W. Park, C.-M. Lee, M. Wakeda, Y. Shibutani, M.L. Falk, J.-C. Lee, *Acta Mater.* 56 (2008) 5440–5450.
- [36] J.C. Qiao, J.M. Pelletier, C. Esnouf, Y.H. Liu, H. Kato, *J. Alloys Compd.* 607 (2014) 139–149.
- [37] H.B. Yu, W.H. Wang, K. Samwer, *Mater. Today* 16 (2013) 183–191.
- [38] A.L. Greer, J.A. Leake, *J. Non-Cryst. Solids* 33 (1979) 291–297.
- [39] C. Chang, H.P. Zhang, R. Zhao, F.C. Li, P. Luo, M.Z. Li, H.Y. Bai, *Nat. Mater.* 21 (2022) 1240–1245.
- [40] M. Beiner, K.L. Ngai, *Macromolecules* 38 (2005) 7033–7042.
- [41] L.T. Zhang, Y.J. Duan, D. Crespo, E. Pineda, Y. Wang, J.-M. Pelletier, J.C. Qiao, *Sci. China-Phys., Mech. Astron.* 64 (2021) 296111.
- [42] R. BoHmer, K.L. Ngai, C.A. Angell, D.J. Plazek, *J. Chem. Phys.* 99 (1993) 4201–4209.
- [43] M.N. Liu, Q. Hao, J.C. Qiao, *J. Non-Cryst. Solids* 564 (2021) 120843.
- [44] J.C. Qiao, Y.H. Chen, R. Casalini, J.M. Pelletier, Y. Yao, *J. Mater. Sci. Technol.* 35 (2019) 982–986.
- [45] W. Zhai, C.H. Wang, J.C. Qiao, J.M. Pelletier, F.P. Dai, B. Wei, *J. Alloys Compd.* 742 (2018) 536–541.
- [46] D.S. Yang, J. Wang, J.M. Pelletier, K.K. Song, J.C. Qiao, *J. Alloys Compd.* 887 (2021) 161392.
- [47] P. Cao, M.P. Short, S. Yip, *Proc. Natl. Acad. Sci. U. S. A.* 114 (2017) 13631–13636.